pected bonding values of about 2.8–3.0 Å, respectively. Indeed, the noncircularity of the electron-density peaks for O* in Figure 2 might result from such displacements. Distances to Sr(2) are either too short (1.48 Å) or too long (<3 Å), and there is no reason to associate an AlO_4* complex with the displacement of this type of Sr atom into the sodalite unit rather than into the large cage.

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Supplementary Material Available: A listing (Table IV) of the observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Mixed-Valence Semiquinone–Catecholate–Iron Complexes

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Abstract: The complex $[Fe(phenSQ)_3]$·phenQ, where phenQ and phenSQ are quinone and semiquinone forms, respectively, of 9,10-phenanthrenequinone, reacts with either 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 5,5′-dimethyl-2,2′-bipyridine (dmbpy) to give complexes of the formulation Fe(phenSQ)(phenCAT)(bidentate nitrogen base). Iron-57 Mössbauer and magnetic susceptibility data indicate that these three complexes are high-spin iron(III) complexes. The mixed-valence character with one semiquinone and one catecholate ($phenCAT^{2-}$) ligand is substantiated by the observation of an intervalence transfer band at 1100 nm in the solid state and in low dielectric constant solvents. In high dielectric solvents there is no IT band and other features are changed, suggesting an *intramolecular* electron transfer to a $Fe^{II}(phenSQ)_2$(bidentate nitrogen base) species. Five analogous compounds can be prepared by the reaction of $Fe(DBSQ)_3$, where DBSQ is the semiquinone form of 3,5-di-*tert*-butyl-1,2-benzoquinone, with bpy, phen, dmbpy, py, and en. These five complexes have the composition Fe^{III}(DBSQ)(DBCAT)(nitrogen base) and are most likely oligomeric in the solid state. No IT bands are seen for these five complexes; however, support for the mixed-valance composition is drawn from infrared spectra.

The interaction between iron centers and quinones plays an important role in bacterial photosynthesis.[3,4] The primary photochemical event in bacterial photosynthesis is a light-induced electron transfer from a primary electron donor to a primary electron acceptor. This event occurs in a bacteriochlorophyl–protein complex called the reaction center where a special bacteriochlorophyl dimer is believed to be the primary electron donor.[5–7] The identity, composition, and mechanism of the primary electron acceptor has been more elusive and is a topic of considerable research. Presently, the primary electron acceptor is believed to a an ubiquinone (Q_I).[3,4,6] Following excitation of the reaction center by a photon, Q_I is reduced to an anionic semiquinone which has been identified by EPR.[4,9] A broad, grossly distorted EPR signal has been observed at $g \sim 1.82$ caused by a weak magnetic interaction with an adjacent iron species. The iron is found to be in the high-spin ferrous state in both the resting and reduced forms of the reaction center, as determined by magnetic susceptibility[10] and ^{57}Fe Mössbauer[11,12] measurements. The iron center is evidently very important to the action of the reaction center since in its absence electrons cannot be shuttled from Q_I to the nearby secondary acceptor quinone, Q_{II}.[13] Secondly, without the presence of iron, Q_I exhibits normal quinone chemistry and acts as a two-electron acceptor. The iron center causes the second redox potential ($Q_I^-\cdot/Q_I^{2-}$) to be of inaccessibly low value[14] and, therefore, has a profound influence on the one-electron shuttling behavior of Q_I. The iron–quinone complex of the reaction center may be usefully described as Q_IFeQ_{II}. The exact environment about these two quinones and about the iron is not well characterized. However, EPR and EXAFS measurements seem to suggest that each of the quinones is in a different environment and is probably not directly bonded to the iron center.[10,15] As electrons are shuttled through the reaction center, several intermediates are formed. They have been detected spectroscopically and their identities postulated to include (Q_IFeQ_{II}), ($Q_I^-\cdot FeQ_{II}$), ($Q_IFeQ_{II}^-\cdot$), and ($Q_I^-\cdot FeQ_{II}^-\cdot$).[3] The last form has proven quite interesting and elusive because the two semiquinones are apparently magnetically coupled in this state. This situation is believed to involve the iron since it is inolved in magnetic interactions with each semiquinone individually and is important in mediating the Q_I–Q_{II} electron transfer.

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A limited number of iron–semiquinone complexes have been prepared and characterized. Three tris(*o*-semiquinone) complexes of high-spin iron(III) have been reported,[16] and the magnetic exchange interaction between each chelating *o*-semiquinone and iron(III) ion was found to be moderately strong ($-J$ is 60–190 cm^{-1}).[17] High-spin iron(III) complexes with a single *o*-semiquinone ligand have also been reported[17,18] to have a moderately strong exchange interaction between paramagnetic ligand and metal ion. The electron-transport quinones are of course *p*-quinones. However, reactions of *p*-quinones with either Fe^{II}(salen),[19] where salen is the dianion of *N,N'*-ethylenebis(salicylideneamine), or Fe^{II}(TPP),[20] where TPP is the dianion of meso-tetraphenylporphyrin, give binuclear iron(III) complexes with bridging hydroquinone dianions. It was the goal of the present work to characterize iron complexes with two *o*-quinone-derived ligands. In this regard it is important to note that Floriani et al.[21] did report two such iron complexes. However, only IR data were used to characterize their two complexes and as such they are not thoroughly characterized.

Experimental Section

Physical Measurements. Variable-temperature (4.2–286 K) magnetic susceptibility data were obtained with a Princeton Applied Research Model 150A vibrating sample magnetometer. A calibrated GaAs diode was used to monitor the sample temperature in conjunction with a $CuSO_4 \cdot 5H_2O$ standard.

Infrared absorption data were obtained with a Perkin-Elmer 599B spectrometer. Samples were studied as KBr pellets or as Fluorolube or Nujol mulls prepared under argon.

Electronic absorption measurements were made on a Cary 14 spectrophotometer with airtight quartz cells or a KBr pellets. Variable-temperature studies between 30–300 K were carried out on solids with Cryogenic Technology, Inc., Spectrim closed-cycle refrigerator, while solutions studied in the range 230–300 K were handled either in glass Dewars with quartz windows or in quartz cells with a gas-cooled sample holder. Temperatures were monitored with an iron–constantan thermocouple.

Electron paramagnetic resonance meaasurements were made on a Varian E-9 spectrometer. Variable-temperature measurements between 350–100 K were made with a Varian gas flow cavity insert, while those at 77 K were obtained with a quartz Dewar made in the School of Chemical Sciences glass shop. Liquid helium spectra were obtained with an Oxford Instruments cavity insert.

Iron-57 Mössbauer spectra were collected on two different spectrometers, both of a constant acceleration type. Isomer shifts are referenced to iron foil at room temperature. Elemental analyses were carried out in the School of Chemical Sciences microanalytical labs.

Compound Preparation. Due to the extreme air sensitivity of many of the products in either the solution and/or the solid state, most reactions were carried out under an atmosphere of purified argon. Argon was passed through 4-Å sieves to eliminate H_2O and purified of O_2 via the use of MnO columns. Schlenk glassware was utilized to prepare Fe(DBSQ)$_3$, [Fe(phenSQ)$_3$]·phenQ, and Fe(DBSQ)(DBCAT)(en). The remaining compounds were prepared in a Vacuum Atmospheres inert-atmosphere box with a He 493 Dri-train. Solvents used in the synthesis and spectroscopic studies were purified prior to use unless otherwise noted. Benzene, toluene, xylene, heptane, THF, and 2MeTHF were distilled from sodium benzophenone under an atmosphere of argon. Dimethylformamide and pyridine were shaken over KOH and then, under argon, refluxed and distilled over BaO. Only the 10–90% cut was taken. Pyridine was further dried over highly activated molecular sieves. Methanol was refluxed and dstilled from magnesium methoxide. Acetone was dried via storage over highly activated molecular sieves. Acetonitrile, dichloromethane, and anisole were reagent grade and used without further purification. All solvents were degassed in vacuo prior to use.

Technical grade 9,10-phenanthrenequinone was purified as the bisulfite addition product[22] and then recrystallizd from ethanol. Iron pentacarbonyl was distilled under argon before use. Unless otherwise noted, other materials were used as purchased without further purification.

Preparative procedures for some of the complexes have appeared previously;[16,21] however, modified preparations were used in most cases.

Fe(DBSQ)$_3$. DBQ (3,5-di-*tert*-butyl-1,2-benzoquinone) (5 g, 22.7 mmol) was dissolved in about 80 mL of anisole; to this solution was added 1.48 g (7.6 mmol) of iron pentacarbonyl. The solution was heated to about 115 °C for 20 h. It was then cooled and the volume was reduced in vacuo to 10 mL and then filtered in air. This procedure gave a purer product than the published procedure using cyclohexane as the solvent.[16]

[Fe(phenSQ)$_3$]·phenQ. PhenQ (9,10-phenanthrenequinone) (5.1 g, 25.0 mmol) was dissolved in about 100 mL of xylene, and then 1.22 g (6.33 mmol) of iron pentacarbonyl was added. The solution was heated in an oil bath to about 115 °C for 36 h. During the first 24 h, the reaction was irradiated with UV light from a General Electric sun lamp. The solution was cooled in a dry ice–acetone bath and then filtered to yield a green microcrystalline product.

[Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ. This compound was prepared via the method of Floriani.[21] [Fe(phenSQ)$_3$]·phenQ (1.1 g, 1.24 mmol) was dissolved in about 50 mL of THF and filtered; to this was added a filtered solution containing 0.4 g (2.56 mmol) of 2,2'-bipyridine (bpy) in 10 mL of THF. The solution was stirred for about 12 h and then heated to reflux for about 10 min and allowed to cool, yielding a beautiful blue-green microcrystalline product. This compund could be recrystallized from THF to again give a crystalline product. The same compound composition is obtained regardless of the stoichiometry of the starting reactants. Good analytical results were obtained for all preparations of the complex. One-half mole of PhenQ was found as a solvate, as confirmed by analytical results and infrared spectroscopy. Anal. Calcd for $C_{45}H_{28}N_2FeO_5$: C, 71.62; H, 4.55; N, 4.08; Fe, 8.12; O, 11.64. Found: C, 70.42; H, 4.41; N, 4.07; Fe, 7.99.

[Fe(phenSQ)(phenCAT)(phen)]·THF. Approximately 0.3 g (0.3 mmol) of [Fe(phenSQ)$_3$]·phenQ was dissolved in 20 mL of THF and filtered. A filtered solution containing 0.12 g (0.61 mmol) of 1,10-phenanthroline (phen) in 20 mL of THF was added. This solution was stirred about 12 h, refluxed for 10 min, and allowed to cool, yielding a green powder. The complex was then suspended in 30 mL of benzene, stirred for about 10 min, filtered, and dried in vacuo. The complex was prepared four separate times to give consistent analysis for one THF solvate molecule. Due to the complexity of the infrared spectrum, no bands could be reliably located and assigned to THF. Anal. Calcd for $C_{44}H_{32}N_2FeO_5$: C, 72.93; H, 4.45; N, 3.87; Fe, 7.71; O, 11.04. Found: C, 71.68; H, 3.94; N, 3.81; Fe, 7.69.

[Fe(phenSQ)(phenCAT)(dmbpy)]·THF. To a filtered THF solution containing 0.3 g (0.3 mmol) of [Fe(phenSQ)$_3$]·phenQ (20 mL) was added a filtered solution of about 0.12 g (0.64 mmol) of dmbpy in 20 mL of THF. The reaction was essentially complete after 10 min since the reaction mixture turns from green to orange with the formation of a green precipitate. The stirred suspension was heated to reflux for about 10 min. After the mixture was cooled, the dark green powder was filtered and washed with about 10 mL of THF and dried in vacuo for about 0.5 h. The compound was found to contain THF as solvent of crystallization. Anal. Calcd for $C_{44}H_{36}N_2FeO_5$: C, 72.53; H, 4.98; N, 3.85; Fe, 7.66; O, 10.98. Found: C, 71.38; H, 4.90; N, 3.96; Fe, 7.53.

Fe(DBSQ)(DBCAT)(bpy). Fe(DBSQ)$_3$ (0.3 g, 0.42 mmol) was dissolved in about 40 mL of toluene and filtered; to this was added a filtered solution of 0.065 g (0.42 mmol) of bpy in 7 mL of toluene. The solution was stirred about 14 h then filtered to yield a blue powder. Additional compound may be obtained by adding more bpy. This compound was made several times, giving a consistently satisfactory analysis each time. The compound may be recrystallized from THF to again obtain a blue powder with the same analytical analysis obtained from toluene. Anal. Calcd for $C_{38}H_{48}N_2FeO_4$: C, 70.25; H, 7.45; N, 4.31; Fe, 8.60; O, 8.60. Found: C, 69.38; H, 7.24; N, 4.41; Fe, 8.78.

Fe(DBSQ)(DBCAT)(phen). Approximately 0.3 g (0.42 mmol) of Fe(DBSQ)$_3$ dissolved in about 40 mL of toluene were filtered and added to a filtered solution of about 0.1 g (0.64 mmol) of phen in 20 mL of toluene. The solution was stirred about 14 h, filtered, washed with 20 mL of toluene, and dried in vacuo. This complex was prepared 3 times with different ratios of starting reagents to yield consistently satisfactory analysis. Anal. Calcd for $C_{40}H_{48}N_2FeO_4$: C, 69.93; H, 7.41; N, 4.29; Fe, 8.56; O, 9.81. Found: C, 71.81; H, 6.96; N, 4.34; Fe, 8.40.

Fe(DBSQ)(DBCAT)(en). Fe(DBSQ)$_3$ (0.232 g, 0.32 mmol) was suspended in about 20 mL of anhydrous methanol. To this solution was added 0.1 mL (1.49 mmol) of freshly distilled ethylenediamine (en). The solution, which turns immediately blue, was stirred for 2 h and filtered

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to give a blue powder which was dried in vacuo for 5 h. Anal. Calcd for $C_{30}H_{48}N_2FeO_4$: C, 64.74; H, 8.69; N, 5.03; Fe, 10.03; O, 11.50. Found: C, 63.97; H, 8.80; N, 4.94; Fe, 9.79.

Fe(DBSQ)(DBCAT)(py). About 0.3 g (0.42 mmol) of Fe(DBSQ)$_3$ was heated to about 50 °C for 10 h in 25 mL of pyridine. The solution was then cooled, allowed to stand for 3 days, filtered, and dried in vacuo. The resulting green powder can be recrystallized from either pyridine or a mixture of pyridine and THF, yielding a dark microcrystalline product. The material was prepared a second time with the reaction carried out at room temperature. This reaction was stirred for about 5 days and then filtered and dried in vacuo. Both samples consistently gave excellent analytical results for only *one* pyridine. Anal. Calcd for $C_{33}H_{45}N_2FeO_4$: C, 68.86; H, 7.88; N, 2.43; Fe, 9.70; O, 11.12. Found: C, 68.53; H, 7.70; N, 2.46; Fe, 9.01.

Fe(DBSQ)(DBCAT)(DMbpy). Fe(DBSQ)$_3$ (0.3 g, 0.42 mmol) was dissolved in about 30 mL of benzene and filtered into a filtered solution containing 0.15 g (0.61 mmol) of dmbpy in 30 mL of benzene. The solution was stirred for 6 h, during which time the solution turned from green to blue. A dark blue precipitate formed and was filtered, washed with 30 mL of benzene, and then dried in vacuo for 30 min. Anal. Calcd for $C_{40}H_{52}N_2FeO_4$: C, 70.58; H, 7.70; N, 4.12; Fe, 8.20; O, 9.40. Found: C, 68.55; H, 7.33; N, 3.77; Fe, 7.45.

Results and Discussion

Compound Formulation and Properties. Three different phenQ complexes were prepared by reacting the tris(*o*-semiquinone) complex [Fe(phenSQ)$_3$]·phenQ in THF with a bidentate nitrogen base. In the following sections it will be shown that these complexes can be best formulated as Fe^{III}(phenSQ)(phenCAT)(bidentate nitrogen base), where phenSQ and phenCAT stand for the semiquinone and catecholate forms, respectively, of 9,10-phenanthrenequinone (phenQ) and the nitrogen base is either 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 5,5′-dimethyl-2,2′-bipyridine (dmbpy). Appreciable quantities of phenQ were isolated in these preparation reactions, indicating the presence of a redox reaction. Since we will show that these complexes most likely contain high-spin Fe(III) ions, the *o*-quinone-derived ligand is present in two different oxidation states. There are two other possible limiting descriptions that can be given to these complexes: Fe^{II}(phenSQ)$_2$(bidentate nitrogen base) or Fe^{III}(phenSQ)$_2$(anionic bidentate nitrogen base radical). Pierpont and Buchanan[23] have summarized the results that indicate that metal complexes with ligands derived from *o*-quinones can be given such limiting descriptions, whereas by contrast the bonding in dithiolene–metal complexes is best described as delocalized.

The three Fe^{III}(phenSQ)(phenCAT)(bidentate nitrogen base) complexes are air stable for a short period of time in the solid state, whereas in solution they react rapidly with oxygen. The phen and dmbpy compounds were consistently isolated as powders with THF as solvent of crystallization, independent of the stoichiometry of reactants. The bpy compound is obtained as a microcrystalline material either directly from the reaction or form a recrystallization in THF. The composition of this microcrystalline compound is [Fe(phenSQ)(phenCAT)(bpy)]·0.5(phenQ). This is the only compound in this paper that has been reported previously; however, Floriani and co-workers[21] did not report the 0.5(phenQ) solvate composition. In the following sections of this paper, data will be presented to show that these three compounds mostly likely consist of monomeric high-spin iron(III) complexes exhibiting a weak *inter*molecular antiferromagnetic exchange interaction in the solid state.

Five different compounds were prepared by the reaction of Fe(DBSQ)$_3$, where DBSQ is the semiquinone form of 3,5-di-*tert*-butyl-1,2-benzoquinone, with the nitrogen bases bpy, phen, dmbpy, pyridine (py), and ethylenediamine (en). In analogy with the phenQ complexes, the four bidentate nitrogen bases gave complexes with the composition Fe(DBSQ)(DBCAT)(bidentate nitrogen base). Interestingly, the product from the reaction with pyridine consistently analyzed as Fe(DBSQ)(DBCAT)(py). Of the five DBQ compounds, only the py complex precipitated as a microcrystalline product. Unfortunately, efforts to grow crystals of this py complex or the microcrystalline phenQ–bpy complex that were suitable for single-crystal X-ray structural work were unsuccessful.

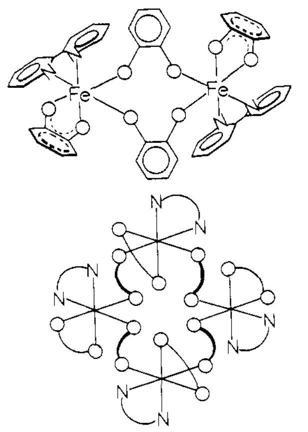

Figure 1. Possible structures for the five Fe(DBSQ)(DBCAT)(nitrogen base) complexes. Catecholate bridging ligands are suggested for the dimeric structure (top). The suggested tetrameric structure (bottom) is only drawn as a sketch where the symbol O⁀O is used to represent either a chelating semiquinone or bridging catecholate ligand. The symbol N⁀N stands for a bidentate nitrogen ligand.

There are a number of reasons to believe that the five DBQ complexes are not monomeric in the solid state. The X-ray structure of Co(DBSQ)(DBCAT)(bpy) has been recently reported.[24] It is a *monomeric* low-spin cobalt(III) complex with coordinated *o*-semiquinone and *o*-catecholate ligands. Although the iron complex that we have prepared appears to be a direct analogue of this cobalt(III) complex, we find that the iron complex exhibits a substantially lower solubility in organic solvents. Variable-temperature magnetic susceptibility results (vide infra) also indicate that Fe(DBSQ)(DBCAT)(bpy) is oligomeric in the solid state. Several transition-metal complexes with *o*-semiquinone and catecholate ligands have been shown to have dimeric and tetrameric structures in the solid state.[23] The compound $Mo_2O_2(DBCAT)_4$, for example, has a dimeric structure with bridging catecholate ligands.[25] A suggested dimeric structure (minus the *tert*-butyl groups) for Fe(DBSQ)(DBCAT)(bpy) is presented in Figure 1. It is also possible that these DBQ compounds assume a tetrameric structure with bridging catecholate ligands as illustrated in Figure 1. The magnetic susceptibility data (vide infra) clearly point to the presence of an even number of iron ions in the molecules.

Mössbauer Data. Mössbauer spectroscopy is a very useful technique for the study of iron complexes. The isomer shift and quadrupole splitting are sensitive to the spin and oxidation state of the iron ion in the absence of appreciable covalency. Spectra were run at 295 and 4.2 K for several of the compounds. Each spectrum showed only a single quadrupole-split doublet. Each spectrum was least-squares fit with two equal-area Lorentzian lines; the fitting data are given in Table I and a few spectra are illustrated in Figure 2.

The spectra obtained for the Fe(dBSQ)(DBCAT)(nitrogen base) complexes consist of single, symmetric, quadrupole-split doublets at both 295 and 4.2 K. The isomer shift values (vs. iron foil) are ~0.46 mm/s at 295 K and 0.56 mm/s at 4.2 K. These values are well within the range of 0.25–0.60 mm/s (vs. iron foil) expected for high-spin iron(III) and are *not* consistent with the values for a high-spin iron(II) complex where the range is expected to be 0.8–1.5 mm/s.[26,27] The slight temperature dependence of the isomer shift is that expected for a second-order Doppler shift. The observed quadrupole splittings are ~1.1–1.2 mm/s, which

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Table I. ^{57}Mössbauer Data[a]

compound	T, K	ΔE_Q, mm/s (vs. Fe)	IS, mm/s	line width,[b] mm/s (low velocity peak)	line width,[b] mm/s (high velocity peak)
[Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ	295	1.271 (10)	0.458 (5)	0.144 (8)	0.185 (14)
	4.2	1.284 (7)	0.564 (3)	0.251 (4)	0.459 (12)
[Fe(phenSQ)(phenCAT)(phen)]·THF	4.2	1.257 (3)	0.577 (1)	0.193 (2)	0.273 (4)
[Fe(phenSQ)(phenCAT)(dmbpy)]·THF	4.2	1.191 (2)	0.572 (1)	0.129 (2)	0.127 (2)
Fe(DBSQ)(DBCAT)(bpy)	295	1.092 (6)	0.477 (3)	0.269 (6)	0.274 (6)
	4.2	1.104 (1)	0.558 (1)	0.141 (1)	0.132 (1)
Fe(DBSQ)(DBCAT)(en)	4.2	1.196 (1)	0.564 (1)	0.135 (1)	0.140 (1)
Fe(DBSQ)(DBCAT)(py)	295	1.046 (4)	0.462 (2)	0.193 (4)	0.187 (4)
	4.2	1.049 (1)	0.579 (1)	0.126 (1)	0.129 (1)
[Fe(phenSQ)$_3$]phenQ[c]	90	1.924 (4)	0.530 (4)	0.245 (4)	0.270 (5)
Fe(DBSQ)$_3$[c]	90	0.752 (2)	0.559 (2)	0.140 (2)	0.133 (2)
Fe(salen)phenSQ[d]	295	0.760 (2)	0.459 (2)	0.175 (2)	0.202 (2)
	4.2	0.792 (2)	0.568 (2)	0.155 (1)	0.151 (1)
Fe(salen)(DBSQ)[d]	295	1.87 (1)	0.40 (1)	0.22 (1)	0.29 (2)
	4.2	0.902 (3)	0.543 (3)	0.217 (3)	0.262 (4)

[a] All of the spectra are from this work except those noted. Peaks were least-squares fit to Lorentzian line shapes; estimated standard deviations are given in parentheses. [b] Full width at half-maximum; spectra were fit with equal areas for both components of a doublet. [c] Buchanan, R. M.; Downs, H. H.; Shorthill, W. B.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* 1978, *100*, 4318. [d] Kessel, S. L.; Emberson, R. M.; Debrunner, P. G.; Hendrickson, D. N. *Inorg. Chem.* 1980, *19*, 1170.

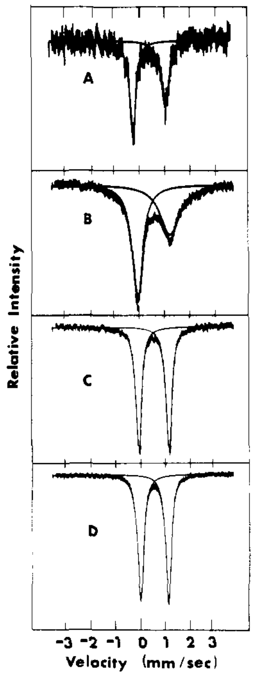

Figure 2. Iron-57 Mössbauer spectra for three of the complexes. Spectra A and B are for Fe(phenSQ)(phenCAT)(bpy)·$^1/_2$phenQ at 295 and 4.2 K, respectively. Spectra C and D, both taken for samples at 4.2 K, are for Fe(DBSQ)(DBCAT)(en) and Fe(DBSQ)(DBCAT)(bpy), respectively.

Table II. Effective Magnetic Moments per Molecule (μ_{eff}/molecule, μ_B)

compound	T, K 286	103	4.2
[Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ	4.90[a]	4.88	5.00
[Fe(phenSQ)(phenCAT)(phen)]·THF	4.99	4.96	3.32
[Fe(phenSQ)(phenCAT)(dmbpy)]·THF	4.52	4.08	0.65
[Fe(DBSQ)(DBCAT)(bpy)]	5.19	4.35	0.49
[Fe(DBSQ)(DBCAT)(dmbpy)]	5.23	4.36	0.69
[Fe(DBSQ)(DBCAT)(phen)]	5.27[a]	4.51	0.51
[Fe(DBSQ)(DBCAT)(en)]	4.00	2.95	0.65
[Fe(DBSQ)(DBCAT)(py)]	3.74	2.63	0.14

[a] Actual temperature is 245 K.

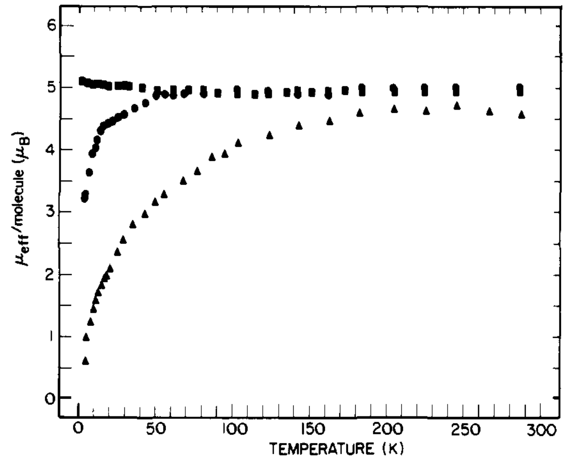

Figure 3. Plots of effective magnetic moments (μ_{eff}) per molecule for solid samples of the Fe(phenSQ)(phenCAT)(nitrogen base) complexes, where the nitrogen base is bpy (■), phen (●), or dmbpy (▲).

is also indicative of high-spin iron(III). Relatively narrow line widths are observed for these complexes indicating only one type of iron site is present.

The isomer shifts and quadrupole splittings for the three phenQ complexes are very similar to those observed for DBQ complexes and again clearly indicate the presence of high-spin Fe(III) ions. There is one difference in the spectra for the two types of complexes. As can be seen in Figure 2, the quadrupole-split doublet for Fe(phenSQ)(phenCAT)(bpy)·0.5phenQ is more symmetric at 295 K than at 4.2 K. The asymmetry in doublets seen for all three of the phenQ complexes most likely reflects the presence of an extended magnetic exchange interaction that is present in these complexes and not in the DBQ complexes. The onset of ordering at low temperatures from the extended exchange interaction leads to a reduced electron-spin relaxation rate which is approximately commensurate with the Larmor precessional frequency of the nucleus. In other words, the spectra are just beginning to turn to a magnetic pattern as a result of the extended interaction and $\pm^1/_2 \rightarrow \pm^3/_2$ component of the doublet is the first to broaden because the $\pm^1/_2 \rightarrow \pm^3/_2$ transitions encompass a larger frequency range than the $\pm^1/_2 \rightarrow \pm^1/_2$ transitions.

Magnetic Susceptibility and EPR Data. No EPR signals were observed for the Fe(DBSQ)(DBCAT)(bpy) or Fe(phenSQ)(phenCAT)(bpy)·$^1/_2$phenQ complexes in the range of 4.2–300 K as either solids, in solution, or in frozen glasses. The absence of an EPR signal is consistent with our formulation of these compounds as high-spin iron(III) complexes, each with one coordinated *o*-semiquinone ligand. It can be concluded that no free semiquinone radicals are present in these compounds.

Variable-temperature (4.2–286 K) magnetic susceptibility data were collected for all eight of the complexes as solids. Some of

Table XI. Theoretical Limiting Values of Spin-Only Effective Magnetic Moment Per Molecule for Different Compound Formulations

	μ_{eff}/molecule, μ_B	
formulation	weak exchange	strong exchange
$Fe^{III}(SQ)(CAT)$(nitrogen base)	6.2	4.9
$Fe^{III}(SQ)_2$(nitrogen base radical)	6.6	2.8
$Fe^{II}(SQ)_2$(nitrogen base)	5.5	2.8

[a] High-spin Fe(III) or Fe(II) ions are assumed and the abbreviations are SQ for *o*-semiquinone monoanion and CAT for *o*-catecholate dianion.

the data are given in Table II; complete data sets appear in Tables III–X.[28]

Plots of effective magnetic moment per molecule (μ_{eff}/molecule) vs. temperature are given in Figure 3 for the three phenQ complexes. The values of μ_{eff}/molecule for Fe(phenSQ)(phenCAT)(nitrogen base), where the nitrogen base is bpy, phen, or dmbpy, are 4.9, 5.0, and 4.5 μ_B, respectively, at room temperature. Furthermore, these μ_{eff}/molecule values are relatively temperature independent between 286 and ~100 K. At temperatures below ~100 K the dmbpy and phen complexes have effective magnetic moments that decrease with decreasing temperature. These characteristics fit best to the Fe^{III}(phenSQ)(phenCAT)(nitrogen base) formulation of these compounds. In the absence of *inter*molecular magnetic exchange interactions, two limiting spin-only effective magnetic moment values can be calculated for each of the three possible formulations of the phenQ complexes. The *intra*molecular antiferromagnetic coupling between the unpaired electrons of a coordinated *o*-semiquinone and those of the metal ion could be either negligible or very strong, leading to two different limiting values of μ_{eff}/molecule. In the case of the Fe^{III}(phenSQ)(phenCAT)(nitrogen base) formulation, for example, an antiferromagnetic exchange interaction between the $S = {}^5/_2$ iron(III) ion and the $S = {}^1/_2$ semiquinone ligand would give an $S = 3$ excited state and an $S = 2$ ground state. If there is a negligible exchange interaction, there would be thermal population in both of these states, and the spin-only value of μ_{eff}/molecule would be 6.2 μ_B. However, a strong exchange interaction between the coordinated semiquinone and the metal would lead to thermal population only in the $S = 2$ ground state and μ_{eff}/molecule equal to 4.9 μ_B. Table XI summarizes the two limiting values of μ_{eff}/molecule for the three different possible formulations of the phenQ complexes. It is clear that the Fe^{III}(phenSQ)(phenCAT)(nitrogen base) formulation *with a strong exchange interaction between semiquinone and Fe(III) ion* fits the high-temperature μ_{eff}/molecule data. This is in agreement with all previous studies[15] of Fe(III)–semiquinone complexes where the exchange interaction has been found to be strong. The decrease in magnetic moment with decreasing temperature for the phen and dmbpy complexes (see Figure 3) is attributable to a weak *inter*molecular antiferromagnetic interaction which grows out of the tendency of these phenQ complexes to stack in the solid state. This type of temperature-dependent μ_{eff}/molecule was seen for $[Fe(phenSQ)_3]$·phenQ where stacking of phenSQ ligands was substantiated by an X-ray crystal structure.[16]

The variable-temperature magnetic susceptibility data for four of the DBQ complexes are illustrated in Figure 4. It should be evident from an examination of this figure and the data in Table II that the magnetic properties of these complexes are apparently more complicated than those for the phenQ complexes. From both steric considerations and the results of previous studies,[17] *inter*molecular magnetic exchange interactions of an appreciable magnitude would *not* be expected for these DBQ complexes. This is obviously due to the two *tert*-butyl substituents on each DBQ ligand. In spite of this, however, we can see in Figure 4 that the value of μ_{eff}/molecule for each of these complexes approaches a value of zero as the sample temperature is decreased to 4.2 K. These complexes are diamagnetic at liquid-helium temperature. It is our opinion that these DBQ complexes are oligomeric with the formulation $[Fe(DBSQ)(DBCAT)(\text{nitrogen base})]_x$, where x is an even number. The reduced solubility of these five iron DBQ complexes compared to the structurally characterized monomeric Co(DBSQ)(DBCAT)(bpy) is further support for the presence of oligomers.

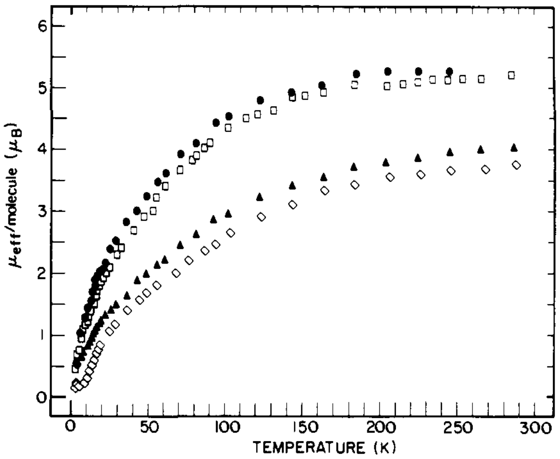

Figure 4. Plots of effective magnetic moments (μ_{eff}) per molecule for solid samples of four of the Fe(DBSQ)(DBCA)(nitrogen base) complexes, where the nitrogen base is bpy (●), phen (□), en (▲), or py (◇).

Infrared Spectra. The infrared spectra of the three Fe(phenSQ)(phenCAT)(nitrogen base) complexes are too complicated to make any conclusions about the state of the coordinated quinone ligands. However, informative spectra were obtained to support the Fe(DBSQ)(DBCAT)(nitrogen base) formulation for the DBQ complexes. Infrared spectra for this latter series of complexes were obtained both for Nujol mulls prepared under argon and for KBr pellets prepared in air. Comparison of the Nujol and KBr spectra indicated that no decomposition occurred in the time required to prepare and run the KBr infrared spectra.

Infrared spectroscopy has proven to be a potent probe in determining the structure of transition metal–quinone complexes.[23] The C=O stretching frequency for free quinones occurs at about 1675 cm^{-1} while, when the quinone is coordinated to a metal ion, a shift of ~60 cm^{-1} to lower energies is observed.[29] Only [Fe(phenSQ)(phenCAT)(bpy)]·$^1/_2$phenQ, which contains a free phenQ molecule, shows a band in the free quinone region, as does $[Fe(phenSQ)_3]$·phenQ.[16] A very important feature of metal–catecholate complexes is the appearance of two rather intense IR bands at ~1480 and ~1250 cm^{-1}. These bands are also observed for free catechols and gain intensity upon coordination to a metal ion. The 1480-cm^{-1} band corresponds to a ring stretching mode, while the 1250-cm^{-1} band is assigned to the C–O stretching frequency.[30] Recent resonance Raman experiments on iron(III)–catecholate complexes indicate important bands at 1572, 1487, 1448, 1359, 1322, and 1154 cm^{-1} for skeletal modes of the substituted ring. Also, a band which can be assigned to the C–O stretching mode is found at ~1260–1267 cm^{-1}. The 1487-cm^{-1} band is very sensitive to the excitation energy and exhibits considerable enhancement. It was concluded that this band has a major contribution from the C–C stretching mode between the coordinated oxygen atoms[31] and is characteristic of the iron–catechol interaction.[32] Transition metal–semiquinone complexes usually have infrared bands attributable to the C$\overset{...}{=}$O stretching modes in the range of ~1420–1460 cm^{-1}. Considerable ring character may also contribute to this band.[30] The C$\overset{...}{=}$O stretch for $Fe(DBSQ)_3$ has been observed at 1455 cm^{-1},[30] while for

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[28] Supplementary material.

[29] Crowley, P. J.; Haendler, H. M. *Inorg. Chem.* **1962**, *1*, 904.

[30] Brown, D. G.; Johnson, W. L., III *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 712.

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[32] Que, L., Jr.; Heistand, R., II *J. Am. Chem. Soc.* **1979**, *101*, 2219.

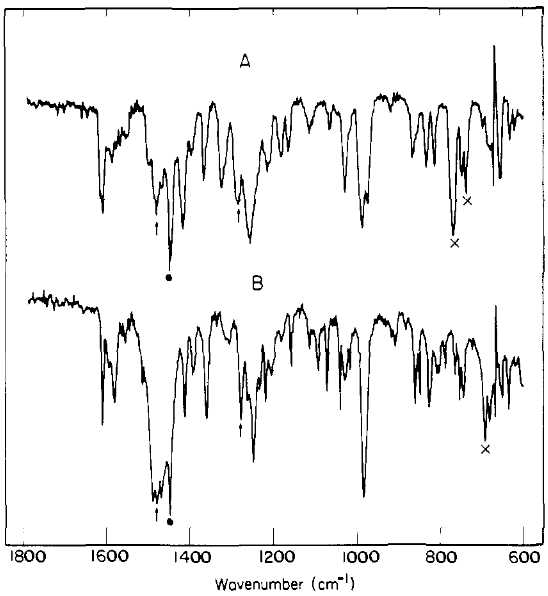

Figure 5. KBr-pellet infrared spectra of Fe(DBSQ)(DBCAT)(bpy) (spectrum A) and Fe(DBSQ)(DBCA)(py) spectrum B). Nitrogen base (X), catecholate (↑), and semiquinone (•) ligand bands are indicated.

Table **XII.** Infrared Data for the Fe(DBSQ)(DBCAT)(nitrogen base) Complexes (cm^{-1})[a]

nitrogen base					
py	bpy	phen	en	Co-bpy	Fe(DBSQ)
1490	1497	1495	1490	1495	
1480	1479	1478	1475	1480	
1468	1468	1468	1462	1470	1470
1448	1449	1449	1440	1452	1455
	1442	1439	1430	1440	
	1427	1419	1419	1420	1420
1410		1410			
1278	1282	1276	1275	1288	
1248	1252	1250	1258	1250	1250
1232			1230		
1221	1210				1221
1200			1205	1200	1200
636	768	832		733	
	736	734		651	

[a] Studied as KBr pellets. Included for comparison are data on Co(DBSQ)(DBCAT)(bpy), prepared by the method of Buchanan and Pierpont (Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* 1980, *102*, 4951), and $Fe(DBSQ)_3$.

$Mn_4(DBSQ)_8$ and $Co_4(DBSQ)_8$ it has been observed at 1426 and 1432 cm^{-1}, respectively. Substantially weaker bands are also observed in the 1250-cm^{-1} region for these three complexes.

The KBr pellet infrared spectra of Fe(DBSQ)(DBCAT)(bpy) and Fe(DBSQ)(DBCAT)(py) are illustrated in Figure 5. The infrared spectrum for the pyridine complex shows a band at 636 cm^{-1}; there is no band at 605 cm^{-1}. This is a clear indication of pyridine coordination to the metal. A band at 756 cm^{-1} is observed for the free bipyridine ligand which has been assigned to the out of plane deformation mode of the two equivalent sets of four hydrogen atoms on the rings. Upon complexation, this band is expected to split into two bands separated by about 30 cm^{-1}.[33] Two bands are observed at 768 and 736 cm^{-1} for Fe(DBSQ)(DBCAT)(bpy) and it can be concluded that the bpy ligand is coordinated.

The IR spectra for the DBQ complexes clearly indicate that the DBQ ligand is present in each of the complexes in both the semiquinone and catecholate forms. The most important bands for four of these complexes are compiled in Table XII. The IR bands for $Fe(DBSQ)_3$ and Co(DBSQ)(DBCAT)(bpy), which has been structurally characterized[24] as having both semiquinone and catecholate ligands, are also listed for comparison purposes. It can be seen that infrared bands characteristic of the catecholate ligand are observed at ~1480 cm^{-1} and in the 1260–1280-cm^{-1} range for the Fe(DBSQ)(DBCA)(nitrogen base) complexes and for the analogous cobalt complex. As expected, these bands are *not* observed for $Fe(DBSQ)_3$ because the catecholate form of the ligand is *not* present. Several infrared bands are observed near 1425–1460 cm^{-1} for the iron–DBQ complexes as well as the one analogous cobalt complex and $Fe(DBSQ)_3$; semiquinone ligands are present in all of these complexes. Unfortunately, the low solubility of the Fe(DBSQ)(DBCAT) complexes precludes obtaining solution-state infrared spectra.

Table XIII. Electronic Absorption Data for the Fe(PhenSQ)(phenCAT)(nitrogen base) Complexes, λ_{max} (nm)

nitrogen base		
bpy	dmbpy	phen
	THF	
1131 sh[a]		1200 sh[b]
1080	1050[a]	1084
755 sh	800 sh	
460	475	472
400	398	398
324	349	348
295	300	
	CH_3CN	
859[b]	802[b]	
532	535	
350	355	
	DMF	
830[b]	802[b]	795[b]
		461
359	365	375
	Toluene	
1118[a]		
940		
831		
442		
346		
304		
	Acetone	
1044[b]		
948		
580		
397		
	KBr (solid)	
1050	1140	1125
484	460	
446		420
408	415	
262		

[a] In matched airtight quartz cells. [b] In airtight glass cells.

Electronic Absorption Spectra. From the data presented in the above sections, it was concluded that the Fe(phenSQ)(phenCAT)(nitrogen base) complexes in the solid state are high-spin Fe(III) complexes, each with both a coordinated semiquinone and a catecholate ligand. If these complexes are indeed mixed-valence molecules, they may exhibit so-called intervalence transfer (IT) bands in the near-IR or visible region. Electronic absorption spectra were obtained for these complexes as solutions dissolved in a variety of solvents and as solids employing KBr pellets. The positions of the observed bands are summarized in Table XIII, and Figure 6 gives typical spectra obtained for the bpy complex both in the solid state and in solutions of THF and DMF.

The dominant feature of the electronic absorption spectra for [Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ in the solid state and in a THF solution is a very broad, low-intensity band in the near-IR region (λ_{max} ~ 1100 nm or 9.1×10^3 cm^{-1} (ϵ ~ 3×10^3 L mol^{-1} cm^{-1})). The other bands seen at approximately 760 nm (sh), 460 nm, 325 nm, and 295 nm are most likely assignable to

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(33) Clark, R. J. H. *J. Chem. Soc.* **1963**, 1377. Bellamy, "The Infrared Spectra of Complex Molecules"; Methuen: London, 1958; p 77.

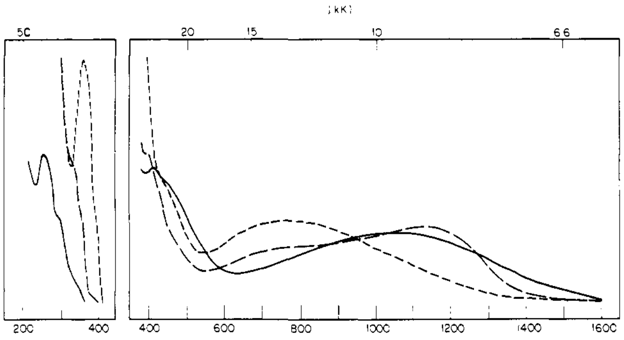

Figure 6. Electronic absorption spectra for [Fe(phenSQ)(phenCAT)(bpy)]·0.5 phenQ run in the following three different media: solid state as KBr pellet (solid line); THF solution (long-dashed line); DMF solution (short-dashed line).

charge-transfer transitions. The 1100-nm band is totally absent from the solution spectra of either $[\mathrm{Fe(phenSQ)_3}]$·phenQ, phenQ, or bpy. The position, shape, and extreme width are clear indications that this 1100-nm band is an intervalence transfer band. The presence of an IT band and the IR data for this compound point to a class II classification for this mixed-valance species. It must be recalled that Co(DBSQ)(DBCAT)(bpy), which has been structurally characterized to be mixed valence with both a semiquinone and a catecholate ligand, has been reported to have an IT band at 1300 nm.[24]

A most interesting observation was made when the electronic absorption spectrum of Fe(phenSQ)(phenCAT)(bpy) was run in DMF. As can be seen in Figure 6, the spectrum obtained in this solvent is quite different from that obtained in THF. The DMF spectrum, for example, has bands at ~830, 430 (sh), 360, and 295 nm. Similar electronic spectral results were obtained for the dmbpy and phen analogues in THF and DMF. Upon exposure to the atmosphere, both the THF and DMF solutions irreversibly decompose to give spectra with the bands expected for the free quinone phenQ and free bipyridine.

The unusual solvent dependence of the spectrum led to a more detailed study for Fe(phenSQ)(phenCAT)(bpy). Electronic absorption spectra were determined in toluene, acetone, acetonitrile, and dimethyl sulfoxide. Spectra obtained for the low dielectric constant solvents toluene and acetone were found to be similar to the results obtained with THF. Likewise, acetonitrile and dimethyl sulfoxide, solvents with high dielectric constants, give spectra similar to that obtained in DMF. The complex was also studied in solutions containing various mixtures of both toluene and DMF. The major observations are as follows: (1) the IT band observed at 1100 nm for the pure toluene solution shifts to higher energies and loses intensity as increasing amounts of DMF are added; (2) as the ratio of DMF to toluene increases, the band at about 800–850 nm, which appears as a shoulder in the pure toluene solution, gains intensity; and (3) no band is observed at 360 nm for a pure toluene solution; however, as the amount of DMF is increased, this band appears and gains intensity. As shown by elemental analysis, [Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ can be recrystallized from DMF to give a product of the same composition and this recrystallized material gives the same spectrum as the unrecrystallized material in either THF, toluene, or the solid state. The complex does not undergo an irreversible change upon dissolution in DMF (or THF).

Table XIV. Electronic Absorption Data for the Fe(DBSQ)(DBCAT)(nitrogen base) Complexes, $\lambda_{\max}$ (nm)

nitrogen base			
bpy	phen	en	py
	THF		
592^a			650^b
405			434
285			372
	DMF		
562^a	610^b		
282	525		
	420		
	340		
	Toluene		
640^b			
	Acetone		
590^b			
	Chloroform		
620^b			
430			
	KBr (solid)		
771	791	671	
540	545	417	
361		387	
295	270	320	
		288	

^{a} In matched airtight quartz cells. ^{b} In airtight glass cells.

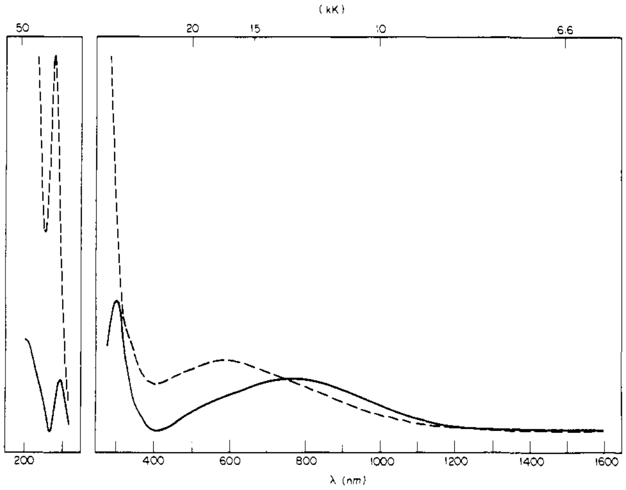

Figure 7. Electronic absorption spectra for Fe(DBSQ)(DBCA)(bpy) determined either in the solid state as a KBr pellet (solid line) or in a THF solution (dashed line).

There are several possible explanations of the unusual solvent dependence observed for [Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ. It is possible that in the higher dielectric solvents the electronic structure of the mixed-valence complex has changed such that the complex is a very localized class I mixed-valence species. The interaction with the solvent changes the coordination geometry somewhat, and the interaction between the semiquinone and catecholate ligands coordinated to the same Fe(III) ion is reduced appreciably. In this case the IT band would be expected to be reduced in intensity and moved to higher energy. A second possible explanation is that in the solid state the complex is in the form of a high-spin Fe(III) complex with one semiquinone and one catecholate ligand, whereas in solution there is an equilibrium established between this Fe(III) form of the complex and an Fe(II) form with two semiquinone ligands coordinated to the iron.

$$\mathrm{Fe^{III}(phenSQ)(phenCAT)(bpy)} \rightleftharpoons \mathrm{Fe^{II}(phenSQ)_2(bpy)}$$

In a low dielectric solvent the equilibrium lies to the left, whereas, in a high dielectric solvent the equilibrium is shifted to the right. Previously, *intra*molecular electron transfers of this type have been noted for $\mathrm{Co(DBSQ)(DBCAT)(bpy)}$[24] and $\mathrm{Mn(DBCAT)_2(py)_2}$.[34] However, in these two cases the change in oxidation state is observed when the temperature of the solution is changed.

Electronic absorption spectra were also obtained for four of the Fe(DBSQ)(DBCAT)(nitrogen base) complexes in solution and in the solid state; the results are given in Table XIV. The spectra for Fe(DBSQ)(DBCAT)(bpy), measured both in the solid state as a KBr pellet and in a THF solution, are given in Figure 7.

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[34] Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1981**, *103*, 3961.

Substantial differences in the two spectra are evident. In THF solutions, bands are seen at ~529, 405, and 285 nm, while in the solid-state bands are seen at ~771, 540 (sh), 361 (sh), and 295 nm. The spectrum of Fe(DBSQ)(DBCAT)(bpy) was also studied in THF solution in the temperature range 300–230 K and in the solid state over the range 300–30 K. However, no new bands or unusual spectral shifts were seen. If Fe(DebSQ)(DBCAT)(bpy) is a mixed-valence complex in the solid state, apparently it does not exhibit absorption in the near-IR associated with an IT band. The appreciable change in the spectrum upon dissolution of the complex in THF could again reflect the type of change in electronic structure seen above for the phenQ complex.

Summary and Cmomments

There Fe(phenSQ)(phenCAT)(nitrogen base) complexes were prepared and characterized to be monomeric high-spin Fe(III) complexes containing both semiquinone and catecholate ligands in the solid state. The mixed-valence character was substantiated, in part, by the observance for solids and for solutions in low dielectric constant solvents of an intervalence transfer band at 1100 nm. In solvents of high dielectric constant, the electronic absorption spectrum undergoes a dramatic change. It is possible that an *intra*molecular electron transfer has occurred to give a $Fe^{II}(phenSQ)_2$(nitrogen base) complex.

The five Fe(DBSQ)(DBCAT)(nitrogen base) complexes prepared in this study were found to be oligomeric high-spin Fe(III) complexes in the solid state; they also each have one semiquinone and one catecholate ligand and are, consequently, mixed valence. Upon dissolution in all organic solvents tested, a dramatic change in the electronic spectrum is seen from that observed for the solids. In both series of complexes, a relatively strong *intra*molecular antiferromagnetic exchange interaction between the unpaired electrons of the metal ion exists.

The above phenQ and DBQ Fe(III) complexes are not yet the best models of the $(Q_I^{-}\cdot FeQ_{II}^{-}\cdot)$ site in bacterial photosynthetic electron transport chains. It is necessary to get better control on the oxidation state of the iron ion. The iron in the site is indicated to be high-spin Fe(II). It should be possible, however, to prepare such a high-spin Fe(II) complex with two semiquinone moieties attached to the ligand framework. Various nitrogeneous macrocyclic ligands and phosphorus ligands could be used to keep the iron in the high-spin divalent state. It is also required for the model that the semiquinone be derived from a *p*-quinone.

Acknowledgment. Support of this research by the National Institutes of Health under Grant HL-13652 is gratefully acknowledged.

Registry No. $Fe(DBSQ)_3$, 64020-89-9; $Fe(phenSQ)_3$, 39797-84-7; Fe(phenSQ)(phenCAT)(bpy), 83573-04-0; Fe(phenSQ)(phenCAT)(phen), 83573-05-1; Fe(phenSQ)(phenCAT)(dmbpy), 83573-06-2; Fe(DBSQ)(DBCAT)(bpy), 83573-07-3; Fe(DBSQ)(DBCAT)(phen), 83573-08-4; Fe(DBSQ)(DBCAT)(en), 83573-09-5; Fe(DBSQ)(DBCAT)(py), 83573-10-8; Fe(DBSQ)(DBCAT)(dmbpy), 83573-11-9; iron pentacarbonyl, 13463-40-6.

Supplementary Material Available: Listing of the variable-temperature magnetic susceptibility data (11 pages). Ordering information is given on any current masthead page.

Competitive Rates of Reactions of Molybdenum Atoms with Arenes

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Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received November 30, 1981*

Abstract: The relative rates of reactions of Mo atoms with arene mixtures at approximately −170 °C are spaced over the small overall range of 3.7 for the following arenes: toluene, *tert*-butylbenzene, *o*-xylene, *α,α,α*-trifluorotoluene, *N,N*-dimethylaniline, fluorobenzene, methyl benzoate, and anisole.

While it is generally assumed that reactions of metal atoms with substrates must have low activation energies if they are to compete successfully with the low-activation-energy process of diffusion and aggregation of bulk metal, there has been no kinetic evidence reported that would test this hypothesis. Low discrimination between a pair of different substrates (competition reactions) would strongly support this hypothesis. We have examined this question with a study of the competition reactions of substituted arenes for molybdenum atoms to give bis(η^6-arene)molybdenum,[1-7]

$$C_6H_5F + C_6H_5R \xrightarrow[-196\ ^\circ C]{Mo} (\eta^6\text{-}C_6H_5F)_2Mo + (\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5R)Mo + (\eta^6\text{-}C_6H_5R)_2Mo \qquad (1)$$

where R is CH_3, 1,2-dimethyl, $C(CH_3)_3$, CF_3, $N(CH_3)_2$, CO_2CH_3, or OCH_3, and have found that the reactions proceed with low discrimination.

The competition reactions between two substituted arenes for molybdenum atoms were conducted by the condensation of a mixture of the two arenes, with a metal to ligand ratio of 20–50:1, at temperatures near −196 °C. The resulting matrix was then warmed to room temperature, and the unreacted substrates were removed by pumping. The mixtures of sandwich compounds were removed from the reactor as ethereal solutions, filtered, and freed of solvent before the crude reaction mixture was analyzed by ^1H and ^{19}F NMR in C_6D_6 at room temperature; from the product distributions, the relative rates of the competition reactions were then determined.

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